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**(54) Air-drying aqueous polymer dispersions**

Lufttrocknende wässrige Polymerdispersionen

Dispersions aqueuses de polymères séchant à l'air

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## Description

The invention relates to an air-drying aqueous polymer dispersion based on a core/shell polymer with an alkyd resin in the core and an addition polymer grafted thereon, to a composite polymer dispersion obtained by emulsion polymerising an addition polymer in the presence of said core/shell polymer, and to coating compositions based on said polymer dispersions.

Air-drying aqueous polymer dispersions based on a core/shell polymer with an alkyd resin in the core and an addition polymer grafted thereon have earlier been proposed in US-A-4 518 724.

The aqueous coating compositions described in this document comprise at least A) one aqueous resin selected from the group of acryl resins, alkyd resins, polyester resins, acryl-modified alkyd resins, and acryl-modified polyester resins, and B) water-insoluble resinous particles having an average particle size of 0,3 to 6  $\mu\text{m}$  obtained by the polymerisation of ethylenically unsaturated compounds, and C) other additives if so desired. Example 39 is the only one in which there is question of a core/shell polymer with an alkyd resin in the core and an addition polymer of styrene, methyl methacrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, and acrylic acid grafted thereon. The proportion of alkyd resin in the core/shell polymer amounts to only 23%, so the properties of a coating composition prepared with this polymer will be affected only slightly by the alkyd resin's presence. It is well-known that coating compositions based on a high percentage of alkyd resin stand out for rapid drying in open air and having a high gloss. However, up to now the known coating compositions which possess the favourable qualities just mentioned have been formulated on an organic solvents basis.

The invention now provides aqueous polymer dispersions based on alkyd resins which, when used in coating compositions, are in no way inferior to the known alkyd resin-containing coating compositions based on organic solvents.

This invention relates to an air-drying aqueous polymer dispersion of the known type mentioned in the opening paragraph wherein 50-90 wt.% of the core/shell polymer is comprised of alkyd resin and 50-10 wt.% is comprised of addition polymer, with the alkyd resin

- containing more than 40 and up to 80 wt.% of unsaturated fatty acid, at least 5 mole% of which contains conjugated double bonds,
- having an acid number of not more than 5 (mg KOH/g), and
- having a number average molecular weight in the range of 400 to 5000, and

with the addition polymer having an acid number in the range of 40 to 200 (mg KOH/g), wherein the core/shell polymer is obtained by the addition polymerisation of radically polymerizable monomers in the presence of the alkyd resin.

In EP-A-O 029 145, an air-drying, aqueous emulsion is disclosed on the basis of polyethylene modified alkyd resins which are subsequently reacted with a copolymer of methacrylic acid, unsaturated acids and compounds having vinyl- or vinylidene groups. The two compounds combine via reaction of the carboxylic groups of the fatty acids and the hydroxyl groups of the alkyd resin.

The aqueous polymer dispersions according to the invention were found to be highly stable and to have a comparatively low viscosity, even at concentrations of 40 wt.% and above. It was found that the properties of topcoats obtained from dispersions with a high alkyd resin content are virtually identical with those of topcoats obtained in a traditional manner using alkyd paints based on organic solvents, the topcoats obtained from the polymer dispersions according to the invention even tending to have superior gloss.

If an alkyd resin of sufficient hydrolytic stability is to be obtained, its acid number must not be higher than 5 (mg KOH/g).

A low acid number for the alkyd resin (<5, preferably <2) may be obtained by, for non-limiting example, conversion with a glycidyl ester of a carboxylic acid or some other mono-epoxide.

With an addition polymer acid number of less than 40, it was found to be impossible to form stable polymer dispersions, while an acid number

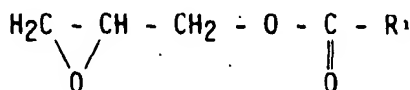
of more than 200 resulted in dispersions which were insufficiently water-resistant.

It is also of importance that the alkyd resin contain more than 40 and up to 80 wt.% of unsaturated fatty acid, since otherwise it will not be possible to obtain topcoats that air-dry at room temperature or 100°C. In this connection it is of importance for at least 5 mole% of unsaturated fatty acids present in the alkyd resin to contain conjugated double bonds for the benefit of the addition polymer's graft polymerisation. Preferably, 10 to 50 mole% of the unsaturated fatty acids will contain conjugated double bonds.

The procedure for preparing the polymer dispersions according to the invention generally is as follows. First, an alkyd resin solution is prepared in an organic solvent. Next, the alkyd resin is grafted to the addition polymer. To obtain a dispersion of sufficient stability it has been found to be advisable in this process to make use of an alkyd resin having a number average molecular weight in the range of 500 to 4000 and a dispersity ( $M_w/M_n$ ) <4, preferably <2.

Particularly suitable aqueous polymer dispersions may be obtained when the alkyd resin is composed of:

- (a) n moles of an aromatic and/or cycloaliphatic dicarboxylic acid or an ester-forming equivalent thereof,  
(b) x moles of a triol having 3-12 carbon atoms, and/or y moles of a tetrafunctional alcohol having 4-13 carbon atoms, with  $x+y=n+1$ ,  
(c) (x+y) to (x+y+2) moles of an unsaturated fatty acid, and  
(d) 2-10 wt.% of a glycidyl ester of a carboxylic acid according to formula (I):

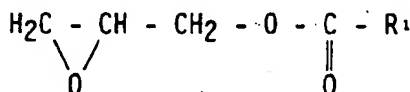


wherein R<sup>1</sup> is an alkyl group having 4-40 carbon atoms.

Here,  $n$  preferably stands for a number in the range of 1 to 5.

Favourable results may also be attained when the alkyd resin is composed of:

- (a) n moles of an aromatic and/or cycloaliphatic tricarboxylic acid or an ester forming equivalent thereof,  
(b) x moles of a diol having 2-12 carbon atoms, and/or y moles of a triol having 3-12 carbon atoms, with  $x+y=2n+1$ ,  
(c)  $(x+y-1)$  to  $(2y+x+1-n)$  moles of an unsaturated fatty acid, and  
(d) 2-10 wt.% of a glycidyl ester of a carboxylic acid according to formula (I):



wherein R<sup>1</sup> represents an alkyl group having 4-40 carbon atoms.

Here,  $n$  preferably stands for a number in the range of 1 to 3.

Examples of suitable cycloaliphatic or aromatic dicarboxylic acids or ester-forming equivalents thereof include: tetrahydrophthalic acid, tetrahydrophthalic anhydride, phthalic anhydride, endomethylene tetrahydrophthalic acid, hexahydrophthalic anhydride, hexachloroendomethylene tetrahydrophthalic acid, hexahydrophthalic acid, hexahydroterephthalic acid, phthalic acid, p-carboxymethyl benzoic acid, dichlorophthalic acid, tetrachlorophthalic acid, dimethyl terephthalate, dimethyl hexahydroterephthalate, naphthalene-2,6-dicarboxylic acid, and diphenyl-o,o'-dicarboxylic acid.

Examples of suitable cycloaliphatic or aromatic tricarboxylic acids or ester-forming equivalents thereof include: 1,2,3-benzene tricarboxylic acid, 1,2,4-benzene tricarboxylic acid, 1,3,5-benzene tricarboxylic acid, trimellitic anhydride, and hexahydrotrimellitic anhydride. The preferred dicarboxylic acids are carboxylic acids having 8-10 carbon atoms, such as isophthalic acid and terephthalic acid. The preferred tricarboxylic acids are trimellitic acid or the anhydride thereof.

When the polymer dispersions are employed in coating compositions that may come into contact with UV-light, it is preferred to make use of cycloaliphatic di- and/or tricarboxylic acids.

Examples of suitable diols for use in the preparation of the alkyd resins to be employed according to the invention include: ethylene glycol, 1,3-propane diol, 1,6-hexane diol, 1,12-dodecane diol, 3-methyl-1,5-pentane diol, 2,2,4-trimethyl-1,6-hexane diol, 2,2-dimethyl-1,3-propane diol, and 2-methyl-2-cyclohexyl-1,3-propane diol.

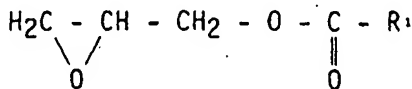
The examples of suitable triols include: glycerol, 1,1,1-trimethylol ethane, and 1,1,1-trimethylol propane. As a suitable tetrafunctional alcohol pentaerythritol may be mentioned.

The number of unsaturated fatty acids eligible for use in the preparation of the alkyd resins to be employed according to the invention is exceedingly large. However, preference is given to the use of mono-and polyunsaturated fatty acids, preferably those containing 12-26 carbon atoms. Specific examples are mono-unsaturated fatty acids, such as myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid, erucic acid, ricinolinic acid; bi-unsaturated fatty acids such as linoleic acid; tri-unsaturated acids, such as linolenic acid, eleostearic acid, and licanic acid; quadri-unsaturated fatty acids, such as arachidonic acid and clupanodonic acid, and other unsaturated fatty acids obtained from animal or vegetable oils. When natural fatty oils are employed, at least 80 wt.% thereof will be made up of the above-mentioned fatty acids or mixtures thereof.

At least 5 mole%, and preferably 10-50 mole%, of the unsaturated fatty acids has conjugated double bonds. One

example of such an acid is conjugated linoleic acid. The optimum amount of fatty acids having conjugated double bonds is closely bound up with the nature of the monomers and initiators used for grafting the addition polymer onto the core.

Low acid numbers (lower than 2 mg KOH/g) and a narrow molecular weight distribution (an Mw/Mn dispersity of less than 2,5) may be obtained by reacting the alkyd having an acid number in the range of 5 to 20 with a mono-epoxide such as 1,2-epoxycyclohexane or, preferably, a glycidyl ester of a carboxylic acid according to formula 1:



wherein R<sup>1</sup> represents an alkyl group having 4-40 carbon atoms.

The alkyd resins suitable for use according to the invention may be obtained by direct esterification of the constituent components, a portion of which may already have been converted into ester diols or polyester diols. Alternatively, the unsaturated fatty acids may be added in the form of a drying oil, such as linseed oil, tunafish oil, dehydrated castor oil, coconut oil, and dehydrated coconut oil. The final alkyd resin is then formed by transesterification with the other added acids and diols. This transesterification is commonly carried out at a temperature in the range of 115° to 250°C, optionally with solvents such as toluene and/or xylene being present. The reaction is generally carried out in the presence of a catalytic amount of a transesterification catalyst. The examples of transesterification catalysts suitable for use include p-toluene sulphonic acid, a basic compound such as an amine, or compounds such as zinc oxide, tetraisopropyl orthotitanate, and triphenylbenzyl phosphonium chloride.

The core/shell polymer is obtained by the addition polymerisation of radically polymerisable monomers in the presence of the alkyd resin described hereinbefore. In this process, the addition polymer is linked to the alkyd resin by means of grafting to the unsaturated conjugated double bond of the fatty acid.

The core/shell polymer prepared according to the invention is easily dispersible in water after an at least partial neutralisation of the carboxyl groups present in the shell of the core/shell polymer with the aid of triethyl amine, dimethyl ethanolamine, KOH, LiOH,  $\text{Li}_2\text{CO}_3$ , or, preferably, with the aid of ammonia and the emulsifying in water of the thus neutralised core/shell polymer.

A wide range of radically polymerisable monomers is available to choose from for the addition polymer chains. Mention may be made in this connection of ethylenically unsaturated monocarboxylic acids, such as (meth)acrylic acid and crotonic acid; (cyclo)alkyl(meth)acrylates having 1-12 carbon atoms in the (cyclo)alkyl group, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, isobornyl(meth)acrylate, dodecyl(meth)acrylate, and cyclohexyl(meth)acrylate; dicarboxylic acids, such as maleic acid (and anhydride), fumaric acid, itaconic acid (and anhydride); (cyclo)alkyl esters of such dicarboxylic acids having 1-12 carbon atoms in the (cyclo)alkyl group, such as dimethyl maleate, diethyl maleate, diethyl fumarate, dipropyl maleate, dibutyl maleate, dibutyl fumarate, 2-ethylhexyl maleate, 2-ethylhexyl fumarate, octyl maleate, isobornyl maleate, dodecyl maleate, and cyclohexyl maleate; (meth)acrylates containing ether groups, such as 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, and 3-methoxypropyl methacrylate; hydroxyalkyl(meth)acrylates, such as 2-hydroxyethyl(meth)acrylate; 2-hydroxypropyl(meth)acrylate, 4-hydroxybutyl acrylate, 6-hydroxyhexyl acrylate, p-hydroxycyclohexyl(meth)acrylate; monovinyl aromatic compounds, such as styrene, vinyl toluene,  $\alpha$ -methyl styrene, and vinyl naphthalene; other substituted (meth)acrylate compounds, such as (meth)acrylamide, (meth)acrylonitrile, N-methylol(meth)acrylamide, and N-alkyl(meth)acrylamides; other mono-unsaturated compounds, such as vinyl chloride, vinyl acetate, vinyl propionate, and vinyl pyrrolidone.

Favourable results were attained with a core/shell polymer of which the shell was obtained from a monomer mixture composed of:

- 20-50 mole% of styrene and/or  $\alpha$ -methyl styrene,  
20-30 mole% of (meth)acrylic acid, and  
20-60 mole% of some other mono-unsaturated compound.

It was found that the stability of the polymer dispersions according to the invention can be increased still further by the incorporation into the core/shell polymer's shell of up to 20 wt.% of a hydroxypolyethylene glycol(meth)acrylate, a hydroxypolyethylene glycol/polypropylene glycol(meth)acrylate, a hydroxypolypropylene glycol(meth)acrylate, or an alkoxy derivative thereof. The molecular weight of the alkoxyalkoxyalkylene groups in these compounds is in the range of 500 to 3000, preferably in the range of 1000 to 2000. Favourable results may likewise be obtained using the reaction product of an alkoxyalkoxyethylene/oxypolypropylene amine and a monoethylenically unsaturated monoisocyanate such as isocyanatoethyl methacrylate and dimethyl-m-isopropenyl benzyl isocyanate.

Needless to say, the selection of the monomers and/or monomer mixtures is dependent on a number of factors, including the hybrid polymer's final application. In actual practice, it is quite easy for the skilled person to take these and other factors into account and adjust the monomers' selection in line with the envisaged use.

The graft polymerisation of the ethylenically unsaturated monomers in the presence of the alkyd resin functionalised with conjugated double bonds is generally carried out in an inert atmosphere (e.g., of nitrogen) in the presence of a radical initiator. The reaction is preferably carried out in a water-miscible organic solvent at a temperature in the range of 60° to 200°C. The amount of organic solvent is usually in the range of 10 to 30 wt.%, calculated on the overall reaction mixture. Suitable examples of such a solvent are glycol ethers and propylene glycol ethers, such as methoxypropanol, butoxyethanol, isopropanol, diethylene glycol monobutyl ether, diethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, propoxypropanol, diethylene glycol dimethyl ether, and N-methyl pyrrolidone. In addition, there may be small amounts of water-immiscible organic solvents, such as ethylmethyl ketone and methyl isobutyl ketone.

Suitable radical initiators include: dibenzoyl peroxide, dicumyl peroxide, methylethyl ketone peroxide, cumene hydroperoxide, tert.butyloxy-2-ethyl hexanoate, tert.butyl perbenzoate, tert.butyl cumyl peroxide, di-tert.butyl peroxide, di-tert.butyl peroxy-3,5,5-trimethyl cyclohexane, and 1,3-bis(tert.butyl)peroxy isopropyl benzene. Also suitable are mixtures of the aforementioned initiators. The selected amount to be used thereof is commonly in the range of about 0,05 to 10 wt.%, preferably in the range of 1 to 5 wt.%, calculated on the overall weight of the monomer mixture.

The invention further relates to an aqueous polymer dispersion in which 10-90 wt.%, preferably at least 30 wt.%, of the solids content is derived from a polymer dispersion according to the invention, and 90-10 wt.%, preferably at least 30 wt.%, is derived from an addition polymer obtained by emulsion polymerisation in the presence of a polymer dispersion according to the invention.

A wide range of mono-ethylenically unsaturated monomers may be used to prepare this addition polymer, including: (cyclo)alkyl(meth)acrylates having 1-12 carbon atoms in the (cyclo)alkyl group, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, octyl(meth)acrylate, isobornyl(meth)acrylate, dodecyl(meth)acrylate, and cyclohexyl(meth)acrylate; monovinyl aromatic compounds, such as styrene, vinyl toluene,  $\alpha$ -methyl styrene, and vinyl naphthalene; other substituted (meth)acrylate compounds, such as (meth)acrylamide, (meth)acrylonitrile, N-methylol(meth)acrylamide, and N-alkyl(meth)acrylamides; other mono-unsaturated compounds, such as vinyl chloride, vinyl acetate, and vinyl propionate. In addition, use may be made in small quantities of: (cyclo)alkyl esters of dicarboxylic acids having 1-12 carbon atoms in the (cyclo)alkyl group, such as dimethyl maleate, diethyl maleate, diethyl fumarate, dipropyl maleate, dibutyl maleate, dibutyl fumarate, 2-ethylhexyl maleate, 2-ethylhexyl fumarate, octyl maleate, isobornyl maleate, dodecyl maleate, and cyclohexyl maleate; (meth)acrylates containing ether groups, such as 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, and 3-methoxypropyl methacrylate; hydroxyalkyl(meth)acrylates, such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 4-hydroxybutyl acrylate, 6-hydroxyhexyl acrylate, p-hydroxycyclohexyl(meth)acrylate, hydroxypolyethylene glycol(meth)acrylates; hydroxypolypropylene glycol(meth)acrylates and alkoxy derivatives thereof.

During the emulsion polymerisation process use may be made of anionic or non-ionic emulsifiers if so desired. The suitable anionic emulsifiers include: potassium laurate, potassium stearate, potassium oleate, sodium decyl sulphate, sodium dodecyl sulphate, sodium dodecyl benzene sulphonate, and sodium rosinate. As examples of non-ionic emulsifiers may be mentioned: linear and branched alkyl polyethylene glycol and alkylaryl polyethylene glycol, polypropylene glycol ethers and thio ethers, alkyl phenoxypoly(ethyleneoxy)ethanols, such as the adduct of 1 mole of nonylphenol and 5-12 moles of ethylene oxide, or the ammonium salt of said adduct's sulphate. During the emulsion polymerisation process use may be made of conventional radical initiators in the usual amounts. The suitable radical initiators include: ammonium persulphate, sodium persulphate, potassium persulphate, bis(2-ethylhexyl)peroxydicarbonate, di-n-butyl peroxydicarbonate, t-butyl perpivalate, t-butyl hydroperoxide, cumene hydroperoxide, dibenzoyl peroxide, dilauroyl peroxide, 2,2'-azobisisobutyronitrile, and 2,2'-azobis-2-methylbutyronitrile. The reducing agents suitable for use together with, say, a hydroperoxide include: ascorbic acid, sodium sulfoxylate, formaldehyde, thiosulphites, bisulphites, hydrosulphites, water-soluble amines, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, N,N'-dimethyl ethanolamine, N,N-diethyl ethanolamine, and reducing salts, such as cobalt sulphate, iron sulphate, nickel sulphate, and copper sulphate. Optionally, a chain length regulator, such as n-octyl mercaptan, dodecyl mercaptan, and 3-mercaptopropionic acid, may be employed.

The component latex derived from polyacrylates and alkyd polymers has a solids content of 30 to 55 wt.%, preferably of about 35 to 50 wt.%.

The aqueous dispersions or emulsions according to the invention are preferably used for the formulation of coating compositions. When employed to this end, the dispersions may contain a variety of other additives common to the paint industry, such as pigments, extenders, dispersing agents, thixotropic and rheological agents, and siccatives. The group of siccatives is commonly taken to include the metal soaps of both alkaline earth metals and heavy metals of monovalent carboxylic acids, such as naphthenic acid, octanoic acid, or 2-ethylhexanoic acid. Independently active

siccatives will contain Co, Mn, Fe, or Ce; to-active siccatives may contain Pb, Ca, Zn, Ba, or Zr. The siccatives are commonly used in an amount of 0,01 to 0,5 wt.%, calculated on the coating composition's solids content. In addition, special emulsifiers may be incorporated into the coating compositions according to the invention in order to attain a spontaneous emulsification in water. Water-emulsifiable siccatives are commercially available. It is easy to determine experimentally which type of siccative will best suit every application. To acquire pot stability, an anti-skinning agent may be incorporated into the coating composition. Examples of anti-skinning agents are oximes, such as butyraldoxime and ethylmethyl ketoxime. In general, favourable results are attained when using an amount each of the siccative and the anti-skinning agent of 0,01 to 1 wt.%, calculated on the amount of film forming constituents.

The coating compositions according to the invention may be applied onto any known substrate, such as wood, synthetic materials, and metals. The suitable application methods include rolling, spraying, sprinkling, dipping, and electrostatic spraying. Needless to say, the coating composition may also be applied by simple brushing.

The coating composition may be dried and cured under a variety of conditions, e.g., at room temperature. Accelerated curing may be accomplished by baking at elevated temperatures in the range of, say, 30° to 80°C over a period of 20 to 60 minutes.

The coating compositions according to the invention may be employed as primer/filler as well as in clear and coloured paints.

The invention will be further illustrated below with reference to the following, non-limiting examples.

In the following examples, the preparation of a number of stable aqueous alkyd emulsions and coating compositions according to the invention is disclosed. The properties measured on these dispersions are listed in Table 1. The dispersions's average particle size given in this table was determined with the aid of dynamic light scattering, with the dispersions diluted to a solids content of about 0,1 wt.%. The viscosity was determined with a Brookfield viscometer (LV - 4; 60 revolutions per minute). The solids content was determined in accordance with ASTM method no. 1644-59, with heating to 140°C over a period of 30 minutes.

#### Preparation of the alkyd resins

##### Alkyd resin A

In a 3 l flask fitted with a stirrer, a thermometer, and a condenser a mixture was homogenised which was composed of:

462 g	of hexahydrophthalic anhydride
536 g	of 1,1,1-trimethylol propane
840 g	of sunflower oil fatty acid (containing 62 wt.% of linoleic acid)
285 g	of unsaturated fatty acid (containing 65 wt.% of conjugated linoleic acid)
0,75 g	of tetra-isopropyl-o-titanate

The contents of the flask were heated to 160°C, at which temperature distillation of the water began. Over a period of 4 hours the temperature was raised to 245°C, the acid number of the contents of the flask at this temperature being kept at <10 (mg KOH/g).

Next, the reaction mixture was cooled to 180°C, and over a period of 30 minutes 100 g of glycidyl ester of 1,1-dimethyl-1-heptane carboxylic acid (Cardura E-10 ex Shell) were added to it. After a reaction time of 1 hour at 180°C the acid number of the reaction mixture was 0,7 (mg KOH/g). The alkyd resin prepared in this manner had an Mw = 3607, Mn = 2016, and a dispersity Mw/Mn = 1,79.

##### Alkyd resin B

In a manner analogous to that disclosed for alkyd resin A, an alkyd resin was prepared from the following constituents:

462 g	of hexahydrophthalic anhydride
536 g	of 1,1,1-trimethylol propane
896 g	of sunflower oil fatty acid (containing 62 wt.% of linoleic acid)
228 g	of unsaturated fatty acid (containing 65% of conjugated linoleic acid)
0,75 g	of tetra-isopropyl-o-titanate
100 g	of glycidyl ester of 1,1-dimethyl-1-heptane carboxylic acid

The thus prepared alkyd resin had an acid number of 0,5 (mg KOH/g), Mw = 3911, Mn = 2137, and a dispersity Mw/Mn = 1,83.

#### Alkyd resin C

In a manner analogous to that disclosed for alkyd resin A, an alkyd resin was prepared from the following constituents:

462 g	of hexahydrophthalic anhydride
536 g	of 1,1,1-trimethylol propane
933,3 g	of sunflower oil fatty acid (containing 62 wt.% linoleic acid)
190 g	of unsaturated fatty acid (containing 65 wt.% of conjugated linoleic acid)
0,75 g	of tetra-isopropyl-o-titanate
100 g	of glycidyl ester of 1,1-dimethyl-1-heptane carboxylic acid

The thus prepared alkyd resin had an acid number of 0,6 (mg KOH/g), Mw = 3861, Mn = 2096, and a dispersity Mw/Mn = 1,84.

#### Alkyd resin D

In a manner analogous to that disclosed for alkyd resin A, an alkyd resin was prepared from the following constituents:

298,8 g	of isophthalic acid
367,2 g	of pentaerythritol
1323,0 g	of sunflower oil fatty acid (containing 62 wt.% of linoleic acid)
192,4 g	of unsaturated fatty acid (containing 65% of conjugated linoleic acid)
1 g	of tetra-isopropyl-o-titanate
100 g	of glycidyl ester of 1,1-dimethyl-1-heptane carboxylic acid

The prepared alkyd resin had an acid number of 1,8 (mg KOH/g), Mw = 6559, Mn = 2488, and a dispersity Mw/Mn = 2,64.

#### Alkyd resin E

In a manner analogous to that disclosed for alkyd resin A, an alkyd resin was prepared from the following constituents:

192 g	of trimellitic anhydride
402 g	of 1,1,1-trimethylol propane
840 g	of sunflower oil fatty acid (containing 62 wt.% of linoleic acid)
285 g	of unsaturated fatty acid (containing 65 wt.% of conjugated linoleic acid)
0,75 g	of tetra-isopropyl-o-titanate
50 g	of glycidyl ester of 1,1-dimethyl-1-heptane carboxylic acid

The prepared alkyd resin had an acid number of 1,9 (mg KOH/g), Mw = 8110, Mn = 2084, and a dispersity Mw/Mn = 3,89.

#### Alkyd resin F

In a manner analogous to that disclosed for alkyd resin A, an alkyd resin was prepared from the following constituents:

277,2 g	of hexahydrophthalic anhydride
367,2 g	of pentaerythritol

(continued)

1209,6 g	of sunflower oil fatty acid (containing 62 wt.% of linoleic acid)
307,8 g	of unsaturated fatty acid (containing 65% of conjugated linoleic acid)
0,9 g	of tetra-isopropyl-o-titanate
100 g	of glycidyl ester of 1,1-dimethyl-1-heptane carboxylic acid

The prepared alkyd resin had an acid number of 1,0 (mg KOH/g), Mw = 4207, Mn = 2321, and a dispersity Mw/Mn = 1,81.

#### Preparation of the alkyd resin/addition polymer dispersions

##### Example I

In a 6 l flask fitted with a stirrer, a thermometer, a reflux condenser, and a dropping funnel, a mixture was homogenised which was composed of:

975 g	of alkyd resin A
180 g	of dipropylene glycol monomethyl ether

The dropping funnel was filled with a homogeneous mixture of:

210,2 g	of styrene
91,0 g	of acrylic acid
101,0 g	of methyl methacrylate
107,6 g	of butyl methacrylate
15,2 g	of di-t-butyl peroxide

After deaeration, the flask and the dropping funnel were brought under a nitrogen atmosphere. The contents of the flask were heated to 135°C, whereupon, with a temperature of 135°C being maintained in the flask, the contents of the dropping funnel were added dropwise in 1 hour. Next, the reaction mixture was kept at this temperature for a further 5 hours, after which the contents of the flask were cooled to 90°C and a homogeneous mixture of

49,4 g	of ammonia (26,1 wt.% NH <sub>3</sub> ) and
300 g	of water

was added, followed by 1720 g of water over a period of 3 hours.

##### Example II

In a manner analogous to that disclosed in Example I, a dispersion was prepared, with the proviso that this time the dropping funnel was filled with a homogeneous mixture of:

210,2 g	of styrene
91,0 g	of acrylic acid
107,6 g	of methyl methacrylate
101,0 g	of butyl methacrylate
15,2 g	of di-t-butyl peroxide

##### Example III

In a manner analogous to that disclosed in Example I, a dispersion was prepared, with the proviso that the mixture in the flask was composed of:

975 g	of alkyd resin A
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(continued)

271 g	of dipropylene glycol monomethyl ether,
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5 and that the dropping funnel this time was filled with a homogeneous mixture of:

260,2 g	of styrene
112,6 g	of acrylic acid
125,1 g	of methyl methacrylate
133,3 g	of butyl methacrylate
18,8 g	of di-t-butyl peroxide

15 On conclusion of the reaction there was added to the contents of the flask at 90°C a homogeneous mixture of:

54,6 g	of ammonia (26,8 wt.% of $\text{NH}_3$ ) and
300 g	of water,

20 followed by the addition of 2025 g of water.

#### Example IV

25 In a manner analogous to that disclosed in Example I, a dispersion was prepared, with the proviso that this time the dropping funnel was filled with a homogeneous mixture of:

200,9 g	of styrene
93,7 g	of acrylic acid
48,3 g	of methyl methacrylate
157,9 g	of butyl methacrylate
24,2 g	of di-t-butyl peroxide

30 The reaction was carried out at 130°C. On conclusion of the reaction there was added to the contents of the flask at 90°C a homogeneous mixture of

49,5 g	of ammonia (26,8 wt.% $\text{NH}_3$ ) and
300 g	of water,

35 followed by the addition of 1917 g of water.

#### Example V

40 In a manner analogous to that disclosed in Example I, a dispersion was prepared, with the proviso that the mixture in the flask was composed of:

325 g	of alkyd resin B
60 g	of dipropylene glycol monomethyl ether,

45 and that the dropping funnel was filled this time with a homogeneous mixture of:

70,1 g	of styrene
30,3 g	of acrylic acid
33,7 g	of methyl methacrylate
35,8 g	of butyl methacrylate
5,1 g	of di-t-butyl peroxide

On conclusion of the reaction there was added to the contents of the flask at 90°C a homogeneous mixture composed of

16,2 g	of ammonia (26,5 wt.% of $\text{NH}_3$ ) and
80 g	of water,

followed by the addition of 591 g of water.

#### Example VI

In a manner analogous to that disclosed in Example V, a dispersion was prepared, with the proviso that the mixture in the flask was composed of:

325 g	of alkyd resin B
50 g	of dipropylene glycol monomethyl ether,

and that the dropping funnel was filled this time with a homogeneous mixture of:

70,1 g	of styrene
30,3 g	of acrylic acid
33,7 g	of methyl methacrylate
35,8 g	of butyl methacrylate
17,5 g	of the reaction product of 1 mole of alkoxypolyoxyethylene/oxypropylene amine and 1 mole of dimethyl-m-isopropenyl benzyl isocyanate
5,1 g	of di-t-butylperoxide

On conclusion of the reaction there was added to the contents of the flask at 90°C a homogeneous mixture of:

16,2 g	of ammonia (26,5 wt.% of $\text{NH}_3$ ) and
80 g	of water,

followed by the addition of 486 g of water.

#### Example VII

In a manner analogous to that disclosed in Example V, a dispersion was prepared, with the proviso that the mixture in the flask was composed of:

350 g	of alkyd resin C
55 g	of dipropylene glycol monomethyl ether,

and that the dropping funnel was filled this time with a homogeneous mixture of:

60,0 g	of styrene
26,0 g	of acrylic acid
28,9 g	of methyl methacrylate
30,8 g	of butyl methacrylate
4,3 g	of di-t-butyl peroxide

On conclusion of the reaction there was added to the contents of the flask at 90°C a homogeneous mixture composed of

13,9 g	of ammonia (26,5 wt.% of $\text{NH}_3$ ) and
80 g	of water,

followed by the addition of 601 g of demineralised water.

#### Example VIII

In a manner analogous to that disclosed in Example II, a dispersion was prepared, with the proviso that in the flask alkyd resin D was substituted for alkyd resin A. Following neutralisation 1816 g of demineralised water were added to the mixture over a period of 3 hours.

#### Example IX

In a manner analogous to that disclosed in Example II, a dispersion was prepared, with the proviso that in the flask alkyd resin E was substituted for alkyd resin A. Following neutralisation 1630 g of demineralised water were added to the mixture over a period of 3 hours.

#### Example X

In a manner analogous to that disclosed in Example I, a dispersion was prepared, with the proviso that in the flask alkyd resin F was substituted for alkyd resin A. Following neutralisation 1542 g of demineralised water were added to the mixture over a period of 3 hours.

#### Example XI

In a manner analogous to that disclosed in Example I, a dispersion was prepared, with the proviso that this time the dropping funnel was filled with a homogeneous mixture of:

204,7 g	of styrene
95,4 g	of acrylic acid
49,2 g	of methyl methacrylate
160,9 g	of butyl methacrylate
14,8 g	of di-t-butyl peroxide

On conclusion of the reaction there was added to the contents of the flask at 90°C a homogeneous mixture of

50,5 g	of ammonia (26,8 wt. % $\text{NH}_3$ ) and
300 g	of water,

followed by the addition of 1719 g of water.

#### Preparation of the composite polymer dispersions

#### Example XII

In a 6 l flask fitted with a stirrer, a thermometer, a reflux condenser, and two dropping funnels, a mixture was homogenised which was composed of:

2127,7 g	of the dispersion of Example III
590,3 g	of water

Dropping funnel A was filled with a pre-emulsion of:

2 g	of sodium dodecyl benzene sulphonate
328 g	of water
680,2 g	of butyl methacrylate
119,8 g	of methyl methacrylate

Dropping funnel B was filled with a homogeneous mixture of:

4 g	of ammonium persulphate
160 g	of water

After deaeration, the flask and the two dropping funnels were brought under a nitrogen atmosphere. The contents of the flask were heated to 80°C, after which, over a period of two hours with this temperature in the flask being maintained, the contents of dropping funnel A and 95% of the contents of dropping funnel B were added to the flask. After the contents of the flask had been kept at 80°C for 30 minutes, the remainder of the contents of dropping funnel B was added to the flask, whereupon the flask was kept at 80°C for a further hour. Next, there was cooling to ambient temperature, and 3 g of ammonia (26,8 wt.% of  $\text{NH}_3$ ) were added.

#### Example XIII

In a manner analogous to that disclosed in Example XII, a composite polymer dispersion was prepared, with the proviso that the mixture in the flask was composed of:

2144,8 g	of the dispersion of Example IV
365,2 g	of water

Dropping funnel A was filled with a pre-emulsion of:

6 g	of sodium dodecyl benzene sulphonate
504 g	of water
972 g	of butyl methacrylate, and
228 g	of methyl methacrylate

Dropping funnel B was filled with a homogeneous mixture of:

6 g	of ammonium persulphate
250 g	of water

Over a period of two hours and 30 minutes, the contents of dropping funnel A and 95% of the contents of dropping funnel B were added to the contents of the flask. On conclusion of the reaction 4,5 g of ammonia (26,8 wt.% of  $\text{NH}_3$ ) were added to the product.

#### Example XIV

In a manner analogous to that disclosed in Example XII, a composite polymer dispersion was prepared, with the proviso that the mixture in the flask was composed of:

2144,7 g	of the polymer dispersion of Example IV
573,3 g	of demineralised water

The properties of the polymer dispersions prepared as specified in the above examples are listed below in Table 1.

TABLE 1

Dispersion of Example	Solids content (wt.%)	Viscosity (Pa.s.)	pH	Average particle size (nm)
I	39,5	0,81	8,1	99
II	39,4	1,29	8,1	89
III	37,6	0,44	8,1	77
IV	37,3	0,36	8,0	65
V	39,5	0,30	7,7	183
VI	44,0	1,42	7,8	320

TABLE 1 (continued)

Dispersion of Example	Solids content (wt.%)	Viscosity (Pa.s.)	pH	Average particle size (nm)
VII	39,0	0,33	7,7	225
VIII	38,8	0,57	8,0	247
IX	40,8	1,49	8,1	167
X	41,2	0,63	7,9	330
XI	39,4	0,46	8,0	336
XII	39,9	0,13	8,0	153
XIII	44,7	0,16	8,1	156
XIV	39,9	0,03	7,9	164

#### Preparation of the coating compositions

The following Examples XV to XXV pertain to a number of pigmented coating compositions according to the invention. These were prepared by the incorporation into the polymer dispersions of Examples I to XI of the following constituents:

- 1) titanium dioxide in such an amount as to give a pigment/polymer weight ratio = 0,65
- 2) water dilutable combination drier containing 3 wt.% of Co, 3 wt.% of Ba, and 5 wt.% of Zr, in an amount of 2 wt.%, calculated on the polymer and pigment contents
- 3) ethylmethyl ketoxime as anti-skinning agent in an amount of 0,5 wt.%, calculated on the polymer content in the polymer dispersion
- 4) a commercially available thickener, Primal RM-8 (ex Rohm & Haas) in an amount of 1 wt.%, calculated on the polymer content in the polymer dispersion.

The mixtures were shaken with glass beads in a Red-devil shaking machine for 30 minutes, after which the glass beads were removed by filtration.

Optionally, there was addition of demineralised water in order to bring the coating composition to the desired viscosity. The coating compositions had a solids content in the range of 40 to 50%.

The pigmented coating compositions according to Examples XXVI to XXVIII were prepared in an analogous manner by the incorporation into the composite polymer dispersions of Examples XII to XIV of the following constituents:

- 1) titanium dioxide in such an amount as to give a pigment/polymer weight ratio = 0,65
- 2) water dilutable combination drier containing 3 wt.% of Co, 3 wt.% of Ba, and 5 wt.% of Zr, in an amount of 1 wt.%, calculated on the polymer and pigment contents
- 3) ethylmethyl ketoxime as anti-skinning agent in an amount of 0,5 wt.%, calculated on the polymer content
- 4) a commercially available thickener, Primal RM-8 (ex Rohm & Haas) in an amount of 0,5 wt.%, calculated on the polymer content
- 5) pigment dispersing agent in an amount of 2,5 wt.%, calculated on the pigment content
- 6) pigment wetting agent in an amount of 1,25 wt.%, calculated on the pigment content
- 7) anti-foaming agent in an amount of 0,3 wt.%, calculated on the polymer content.

After a maturing period of at least 24 hours the pigmented coating compositions were applied onto a steel panel (Bonder 132) pretreated with zinc phosphate and onto a sheet of glass in a layer thickness of 30 to 40  $\mu$ m (after curing).

After 1 week of drying at ambient temperature the hardness on the steel panel and the gloss and the water resistance on the sheet of glass were determined. The results are compiled in Table 2. After 8 weeks of drying at ambient temperature the hardness and also the flexibility on the steel panel were determined, the results of the measurements being listed in Table 3. Tables 2 and 3 further include the test results for two pigmented commercially available resins. Of these, Ref. 1 is based on a white spirit-containing alkyd resin and Ref. 2 is based on a water-dilutable acrylic emulsion.

The properties listed in the tables below were determined as follows: The Persoz Hardness was determined in accordance with French industrial standard method NF T30-016, the result being expressed in seconds. An acceptable minimum is about 40 seconds. The flexibility of the coating compositions was determined with the ball impact test in accordance with ASTM D2794-69 using a ball weight of 0,908 kg, a ball diameter of 15,9 mm, and an aperture of 16,3 mm. The results are expressed in kg.cm. An acceptable minimum flexibility for the coated side is 35 kg.cm, the maximum measurable value being 85 kg.cm.

In addition, the Erichsen indentation test was carried out, the results being expressed in mm: a value >6 indicates a flexible topcoat, while a value of 2 in this test indicates that the topcoat is brittle.

The gloss was determined in accordance with ASTM D-523 at 60° and 20°. A gloss value on a sheet of glass of above 80 at 60° is considered high, while a gloss value of above 90 at 60° is considered very high.

The water resistance was determined by immersion in a water-bath of 20°C for 24 hours, attention being paid to the film's softening and the regeneration time. The test is rated on a 1-10 scale, where "1" is very poor and "10" is excellent.

TABLE 2

	topcoat based on the pigmented coating composition of example	coating composition based on example	properties after 1 week			
			on steel		on glass	
			Persoz hardn. (sec.)	water resistance	gloss	
					60°	20°
	XV	I	70	9	91	82
	XVI	II	72	9	90	80
	XVII	III	75	9	92	84
	XVIII	IV	50	9	93	83
	XIX	V	68	8	90	80
	XX	VI	50	7	94	85
	XXI	VII	56	8	88	74
	XXII	VIII	65	9	86	72
	XXIII	IX	50	9	86	72
	XXIV	X	65	9	84	58
	XXV	XI	55	9	88	64
	XXVI	XII	90	8	88	66
	XXVII	XIII	98	8	84	58
	XXVIII	XIV	92	8	86	62
	Ref. 1		70	9	89	80
	Ref. 2		82	5	80	55

The results listed in Table 2 show that, for a number of compositions, the topcoats applied using the coating compositions according to the invention have even higher gloss than the topcoats applied using the known coating compositions. Moreover, the water resistance of the topcoats using the coating compositions according to the invention ranges from high to very high.

TABLE 3

	topcoat based on the pigmented coating composition of example	coating composition based on example	properties after 8 weeks			
			on steel			
			Persoz hardn. (sec.)	flexibility (kg.cm)		Erichsen indentation (mm)
				coated side	uncoated side	
	XV	I	108	28	8	> 9
	XVI	II	110	28	8	8,9
	XVII	III	127	28	8	8,7
	XVIII	IV	86	30	6	> 9
	XIX	V	98	30	6	> 9

The results listed in Table 3 show that the mechanical properties of the topcoats applied using the coating compositions according to the invention are as high as or even superior to those of the topcoats applied using the known coating compositions.

1. An air-drying aqueous polymer dispersion based on a core/shell polymer with an alkyd resin in the core and an addition polymer grafted thereon, characterised in that 50-90 wt.% of the core/shell polymer is comprised of alkyd resin and 50-10 wt.% is comprised of addition polymer, with the alkyd resin

- with the addition polymer having an acid number in the range of 40 to 200 (mg KOH/g), wherein the core/shell polymer is obtained by the addition polymerization of radically polymerizable monomers in the presence of the alkyd resin.

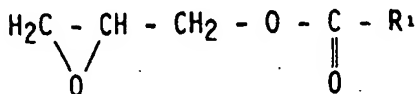
- (a) n moles of an aromatic and/or cycloaliphatic dicarboxylic acid or ester-forming equivalent thereof,  
(b) x moles of a triol having 3-12 carbon atoms, and/or y moles of a tetrafunctional alcohol having 4-13 carbon atoms, with  $x+y=n+1$ ,  
(c)  $(x+y)$  to  $(x+y+2)$  moles of an unsaturated fatty acid, and  
(d) 2-10 wt.% of a glycidyl ester of a carboxylic acid according to formula (I):



wherein R<sup>1</sup> is an alkyl group having 4-40 carbon atoms.

- 3. A polymer dispersion according to claim 1, characterised in that the alkyd resin is comprised of:**

- (a) n moles of an aromatic and/or cycloaliphatic tricarboxylic acid or ester-forming equivalent thereof,  
(b) x moles of a diol having 2-12 carbon atoms, and/or y moles of a triol having 3-12 carbon atoms, with  $x+y=2n+1$ ,  
(c) (x+y-1) to (2y+x+1-n) moles of an unsaturated fatty acid, and  
(d) 2-10 wt.% of a glycidyl ester of a carboxylic acid according to formula (I):



wherein R<sup>1</sup> represents an alkyl group having 4-40 carbon atoms.

4. A polymer dispersion according to one or more of the preceding claims, characterised in that the alkyd resin has a number average molecular weight in the range of 500 to 4000 and a dispersity ( $M_w/M_n$ )  $<4$ , preferably  $<2$ .
5. A polymer dispersion according to one or more of the preceding claims, characterised in that the acid number of the alkyd resin is  $<5$ , preferably  $<2$ , through conversion with a glycidyl ester of a carboxylic acid or some other mono-epoxide.
6. A polymer dispersion according to one or more of the preceding claims, characterised in that the shell is obtained from a monomer mixture comprised of:
  - 20-50 mole% of styrene and/or  $\alpha$ -methyl styrene,
  - 20-30 mole% of (meth)acrylic acid, and
  - 20-60 mole% of some other mono-unsaturated compound.
7. A polymer dispersion according to one or more of the preceding claims, characterised in that into the shell there is incorporated up to 20 wt.% of a hydroxypolyethylene glycol(meth)acrylate, hydroxypolyethylene glycol/polypropylene glycol(meth)acrylate, hydroxypolypropylene glycol(meth)acrylate or alkoxy derivative thereof, or some other unsaturated monomer containing hydroxy- or alkoxyalkylene groups having an  $M_n$  in the range of 500 to 3000.
8. A polymer dispersion according to one or more of the preceding claims, characterised in that at least a portion of the addition polymer's carboxyl groups is neutralised.
9. A polymer dispersion in which 10-90 wt.%, preferably at least 30 wt.%, of the solids content is derived from a polymer dispersion according to one or more of the preceding claims and 90-10 wt.%, preferably at least 30 wt.%, is derived from an addition polymer obtained by emulsion polymerisation in the presence of any one of the polymer dispersions claimed hereinbefore.
10. A coating composition, characterised in that it is based on an aqueous polymer dispersion according to one or more of the preceding claims.

## Patentansprüche

1. Lufttrocknende wässrige Polymerdispersion auf Basis eines Kern/Schalen-Polymers mit einem Alkydharz im Kern und einem darauf aufgepfropften Additionspolymer, dadurch gekennzeichnet, dass 50-90 Gew.% des Kern/Schalen-Polymers aus Alkydharz und 50-10 Gew.% aus Additionspolymer bestehen, wobei das Alkydharz
  - mehr als 40 und bis zu 80 Gew.% ungesättigte Fettsäure enthält, wovon mindestens 5 Mol% konjugierte Doppelbindungen enthalten,
  - eine Säurezahl von nicht mehr als 5 (mg KOH/g) und

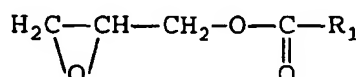


ein Zahlenmittel-Molekulargewicht im Bereich von 400 bis 5000 hat, und

wobei das Additionspolymer eine Säurezahl im Bereich von 40 bis 200 (mg KOH/g) besitzt und das Kern/Schalen-Polymer durch Additionspolymerisation von radikalisch polymerisierbaren Monomeren in Gegenwart des Alkydharzes erhalten ist.

2. Polymerdispersion nach Anspruch 1, dadurch gekennzeichnet, dass das Alkydharz besteht aus:

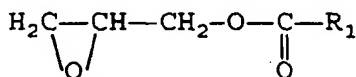
- (a) n Mol einer aromatischen und/oder cyclo aliphatischen Dicarbonsäure oder einem esterbildenden Äquivalent hiervon,
- (b) x Mol eines Triols mit 3-12 Kohlenstoffatomen und/oder y Mol eines tetrafunktionellen Alkohols mit 4-13 Kohlenstoffatomen, wobei  $x+y=n+1$  ist,
- (c)  $(x+y)$  bis  $(x+y+2)$  Mol einer ungesättigten Fettsäure und
- (d) 2-10 Gew.% eines Glycidylesters einer Carbonsäure gemäss der Formel (I):



worin  $\text{R}_1$  eine Alkylgruppe mit 4-40 Kohlenstoffatomen ist.

3. Polymerdispersion nach Anspruch 1, dadurch gekennzeichnet, dass das Alkydharz besteht aus:

- (a) n Mol einer aromatischen und/oder cyclo aliphatischen Tricarbonsäure oder einem esterbildenden Äquivalent hiervon,
- (b) x Mol eines Diols mit 2-12 Kohlenstoffatomen und/oder y Mol eines Triols mit 3-12 Kohlenstoffatomen, wobei  $x+y=2n+1$ ,
- (c)  $(x+y-1)$  bis  $(2y+x+1-n)$  Mol einer ungesättigten Fettsäure und
- (d) 2-10 Gew.% eines Glycidylesters einer Carbonsäure gemäss der Formel (I):



worin  $\text{R}_1$  eine Alkylgruppe mit 4-40 Kohlenstoffatomen darstellt.

4. Polymerdispersion nach einem oder mehreren der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das Alkydharz ein Zahlenmittelmolekulargewicht im Bereich von 500 bis 4000 und eine Dispersität ( $M_w/M_n$ )  $<4$ , vorzugsweise  $<2$  hat.

5. Polymerdispersion nach einem oder mehreren der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Säurezahl des Alkydharzes  $<5$ , vorzugsweise  $<2$  erhalten wird durch Konversion mit einem Glycidylester einer Carbonsäure oder einem anderen Monoepoxid.

6. Polymerdispersion nach einem oder mehreren der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Schale aus einer Monomermischung erhalten wird, die besteht aus:

- 20-50 Mol% Styrol und/oder  $\alpha$ -Methylstyrol,
- 20-30 Mol% (Meth)acrylsäure und
- 20-60 Mol% einer anderen mono-ungesättigten Verbindung.

7. Polymerdispersion nach einem oder mehreren der vorangehenden Ansprüche, dadurch gekennzeichnet, dass in die Schale bis zu 20 Gew.% eines Hydroxypolyethylenglykol(meth)acrylates, Hydroxypolyethylenglykol/Polypropylenglykol(meth)acrylates, Hydroxypolypropylenglykol(meth)acrylates oder Alkoxyderivates hiervon oder ein anderes ungesättigtes Monomer, das Hydroxy- oder Alkoxyalkoxyalkylengruppen mit einem Mn im Bereich von 500 bis 3000 einverleibt enthält.

8. Polymerdispersion nach einem oder mehreren der vorangehenden Ansprüche, dadurch gekennzeichnet, dass mindestens ein Teil der Carboxylgruppen des Additionspolymeren neutralisiert sind.
9. Polymerdispersion, in der 10-90 Gew.%, vorzugsweise mindestens 30 Gew.%, des Feststoffgehaltes von einer Polymerdispersion gemäss einem oder mehreren der vorangehenden Ansprüche abgeleitet ist und 90-10 Gew.%, vorzugsweise wenigstens 30 Gew.%, von einem Additionspolymer abgeleitet ist, das durch Emulsionspolymerisation in Gegenwart von einer oder mehreren der obenstehend beanspruchten Polymerdispersionen erhalten ist.
10. Beschichtungsmittel, dadurch gekennzeichnet, dass seine Basis eine wässrige Polymerdispersion gemäss einem oder mehreren der vorangehenden Ansprüche ist.

## Revendications

1. Une dispersion aqueuse de polymères séchant à l'air à base de polymère à noyau/enveloppe avec une résine alkyde dans le noyau sur laquelle est greffé un polymère d'addition, caractérisée en ce que 50 à 90% en poids du polymère à noyau/enveloppe comprennent de la résine alkyde et 50 à 10% en poids comprennent du polymère d'addition.

avec la résine alkyde qui :

- contient plus de 40 et jusqu'à 80% en poids d'acide gras insaturé, dont au moins 5% en moles contiennent des doubles liaisons conjuguées,
- a un indice d'acide ne dépassant pas 5 mg de KOH/g, et
- a un poids moléculaire moyen en nombre dans la gamme de 400 à 5.000, et

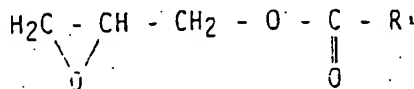
avec le polymère d'addition qui :

- a un indice d'acide dans la gamme de 40 à 200 mg de KOH/g,

dans laquelle le polymère à noyau/enveloppe est obtenu par la polymérisation par addition de monomères polymérisables radicalairement en présence de la résine alkyde.

- 2. Une dispersion de polymères suivant la revendication 1, caractérisée en ce que la résine alkyde comprend:**

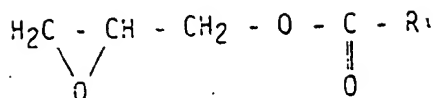
- (a) n moles d'un acide dicarboxylique aromatique et/ou cycloaliphatique ou un équivalent de celui-ci formant un ester,
- (b) x moles d'un triol ayant 3 à 12 atomes de carbone, et/ou y moles d'un alcool tétrafonctionnel ayant 4 à 13 atomes de carbone, avec  $x + y = n + 1$ ,
- (c)  $(x + y)$  à  $(x + y + 2)$  moles d'un acide gras insaturé, et
- (d) 2 à 10% en poids d'un ester glycidyle d'un acide carboxylique représenté par la formule (1):



dans laquelle R<sup>1</sup> est un groupe alkyle ayant 4 à 40 atomes de carbone.

3. Une dispersion de polymères suivant la revendication 1, caractérisée en ce que la résine alkyde comprend de :

- (a) n moles d'un acide tricarboxylique aromatique et/ou cycloaliphatique ou d'un équivalent estérifiant de celui-ci,  
(b) x moles d'un diol ayant 2 à 12 atomes de carbone, et/ou y moles d'un triol ayant 3 à 12 atomes de carbone, avec  $x + y = 2n + 1$ ,  
(c)  $(x + y - 1)$  à  $(2y + x + 1 - n)$  moles d'un acide gras insaturé, et  
(d) 2 à 10% en poids d'un ester glycidylique d'un acide carboxylique représenté par la formule (1):



dans laquelle R<sup>1</sup> est un groupe alkyle ayant 4 à 40 atomes de carbone.

4. Une dispersion de polymères suivant l'une ou plusieurs des revendications précédentes, caractérisée en ce que la résine alkyde a un poids moléculaire moyen en nombre compris dans la gamme de 500 à 4.000 et une polydispersité M<sub>w</sub>/M<sub>n</sub> inférieure à 4, de préférence inférieure à 2.
5. Une dispersion de polymères suivant l'une ou plusieurs des revendications précédentes, caractérisée en ce que l'indice d'acide de la résine alkyde est inférieur à 5, de préférence inférieur à 2, par conversion avec un ester glycidyle d'un acide carboxylique ou tout autre mono-époxy.
6. Une dispersion de polymères suivant l'une ou plusieurs des revendications précédentes, caractérisée en ce que l'enveloppe est obtenue à partir d'un mélange de monomères comprenant de :
  - 20 à 50% en moles de styrène et/ou d'α-méthyl styrène,
  - 20 à 30% en moles d'acide (méth)acrylique, et
  - 20 à 60% en moles de quelque autre composé mono-insaturé.
7. Une dispersion de polymères suivant l'une ou plusieurs des revendications précédentes, caractérisée en ce que dans l'enveloppe, il est incorporé une quantité allant jusqu'à 20% en poids d'un (méth)acrylate d'hydroxypolyéthylène glycol, d'un (méth)acrylate d'hydroxypolyéthylène glycol/polypropylène glycol, d'un (méth)acrylate d'hydroxypolypropylène glycol, ou d'un dérivé alcoxy de ceux-ci, ou de tout autre monomère insaturé contenant des groupes hydroxy ou alcoxypolyoxyalkylènes ayant un poids moléculaire compris dans la gamme de 500 à 3.000.
8. Une dispersion de polymères suivant l'une ou plusieurs des revendications précédentes, caractérisée en ce qu'une partie au moins des groupes carboxy du polymère d'addition est neutralisée.
9. Une dispersion de polymères, dans laquelle 10 à 90% en poids, de préférence au moins 30% en poids de la teneur en solides proviennent d'une dispersion de polymères suivant l'une ou plusieurs des revendications précédentes, et 90 à 10% en poids, de préférence au moins 30% en poids, proviennent d'un polymère d'addition obtenu par polymérisation en émulsion en présence de l'une quelconque des dispersions de polymère revendiquées plus haut.
10. Une composition de revêtement, caractérisée en ce qu'elle est à base d'une dispersion aqueuse de polymères suivant l'une ou plusieurs des revendications précédentes.